clear oil: ^{1}H NMR (200 MHz) δ 6.2–6.5 (2 H, m), 4.25 (2 H, q, J = 7 Hz), 3.68 (0.6 H, t, J = 6.9 Hz), 3.62 (0.4 H, t, J = 7 Hz), 2.91 (0.6 H, m), 2.70 (0.4 H, m), 1.26 (3 H, t, J = 7 Hz); IR (neat) 3080, 2260, 1745, 1645 cm^{-1}.

Reaction of 52 with Bu_3SnH. Following the general high-dilution reaction procedure C, bromide **52a** (230 mg, 1.0 mmol) was treated with Bu_3SnH (270 μL, 1.0 mmol) and AIBN (8 mg, 0.05 mmol). The crude residue isolated after workup was purified by flash chromatography. Initial elution with 10% ethyl acetate/hexane afforded 49 mg (32%) of a 1:1 mixture of **ethyl (*E* or *Z*)-5-cyano-4-pentenoate (53)** as a clear oil: ^{1}H NMR (300 MHz) δ 6.70 (0.5 H, dt, J = 16, 7 Hz), 6.51 (0.5 H, dt, J = 10.5, 7.5 Hz), 5.4 (1 H, m), 4.13 (2 H, broad q, J = 7 Hz), 2.4–2.8 (4 H, m), 1.25 (3 H, t, J = 7 Hz); ^{13}C NMR δ 171.6 (2 × s), 153.4 (d), 152.6 (d), 118.7 (s), 100.9 (d), 100.7 (d), 60.8 (t), 60.7 (t), 32.5 (t), 31.9 (t), 28.2 (t), 26.9 (t), 14.1 (2 × q); IR (neat) 3060, 2220, 1730, 1640 cm^{-1}; m/e 153 (5), 108 (63), 107 (48), 80 (88). Further elution afforded 54 mg (23%) of recovered starting material.

Registry No. 14, 107408-19-5; **18**, 620-79-1; **20**, 112818-02-7; **21**, 59803-41-7; **24**, 112818-03-8; **25a**, 112818-04-9; **25b**, 112211-71-9; **25c**, 112211-69-5; **29a**, 50984-08-2; **29b**, 112211-72-0; **29c**, 112818-05-0; **30a**, 112818-06-1; **30b**, 112211-73-1; **33a** (isomer 1), 112818-07-2; **33a** (isomer 2), 112818-08-3; **33b** (isomer 1), 112818-09-4; **33b** (isomer 2), 112818-10-7; **34a**, 112818-11-8; **34b**, 2900-10-9; **34c**, 112211-75-3; **34d**, 112818-12-9; **34e**, 112818-13-0; **34f**, 112211-76-4; **34g**, 112818-14-1; **37a**, 5453-88-3; **37b**, 7500-91-6; **37c**, 68081-50-5; **37d**, 112818-15-2; **38a**, 33668-25-6; **38b**, 37746-13-7; **38c**, 17606-96-1; **38d**, 112211-77-5; **39a**, 17094-21-2; **39b**, 82072-34-2; **40a**, 112818-16-3; **40c**, 112818-17-4; **41a**, 32811-25-9; **41b**, 112818-18-5; **42a**, 112818-16-3; **42b**, 77216-64-9; **45**, 74023-52-2; **48a**, 112818-19-6; **48b**, 110528-50-2; **48c**, 110528-54-6; **48d**, 61114-31-6; **48e**, 61777-25-1; **49a**, 2616-94-6; **49b**, 112818-20-9; **50a**, 112818-21-0; **50b**, 74036-93-4; **51**, 112818-22-1; **52**, 112818-23-2; **53**, 112818-24-3; $AcCH_2CO_2Et$, 141-97-9; *o*-$BrC_6H_4CH_2Br$, 3433-80-5; $NCCH_2CO_2Et$, 105-56-6; $BrCH_2SePH$, 60466-50-4; $ClCH_2SePh$, 83442-19-7; ICH_2I, 83442-19-7; $EtCO_2Me$, 554-12-1; ClCOSEt, 2941-64-2; $Br(CH_2)_2Me$, 106-94-5; $Br(CH_2)_4Br$, 110-52-1; BrBu, 109-65-9; $BrCH{=}CHCH_2Br$, 627-15-6; $BrCH_2CH{=}CH_2$, 106-95-6; ethyl 2-oxocyclopentane-1-carboxylate, 611-10-9; methyl 2-oxocyclohexane-1-carboxylate, 41302-34-5; methyl 2-oxocyclooctane-1-carboxylate, 5452-73-3; methyl 2-oxocycloheptane-1-carboxylate, 52784-32-4; 1-(trimethylsilyl)oxy)cyclohexene, 6651-36-1; 2-methylcyclohexanone, 583-60-8; methyl 2-oxocyclopentane-1-carboxylate, 10472-24-9.

A General Method for the Preparation of Carbonyl Compounds and Butenolides from Organomanganese Pentacarbonyl Complexes†[1]

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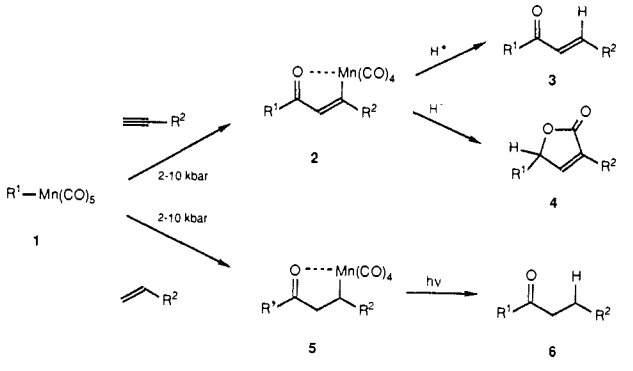
Abstract: Sequential insertion of carbon monoxide and either alkenes or alkynes into alkylmanganese pentacarbonyl complexes at high pressures (2–10 kbar) provided acyl-coordinated manganese complexes (manganacycles) in good yields. Unsymmetrical alkenes and alkynes displayed high regioselectivity in the insertion reaction. The resulting manganese complexes are valuable intermediates in the preparation of organic compounds. For instance, the adducts obtained from alkynes were demetalated under acidic conditions to give *E*-enones. Alternatively, hydride reduction of these adducts afforded butenolides by an intramolecular Reppe reaction. Photochemical demetalation of the alkene-derived manganacycles provided ketones. X-ray and chemical evidence is presented which demonstrates that the manganacycles derived from alkyne insertion are aromatic and should be depicted as metallafuran derivatives.

The insertion of transition metal–carbon bonds into carbon–carbon or carbon–oxygen multiple bonds is a key reaction in many heterogeneous and homogeneous transition metal catalyzed processes.[2-4] Migratory insertion of alkylmanganese pentacarbonyl complexes (**1**) is an excellent model for insertion of carbon monoxide into transition metal–alkyl bonds and this process has been investigated by Calderazzo,[5] Casey,[6] Flood,[7] and others.[8,9] As part of these studies, Pruett et al. demonstrated that electron-withdrawing substituents attached to the alkyl residue retarded the rate of migratory insertion in the manganese complexes.[8h] For instance, methyl manganese pentacarbonyl (**1**: R = Me) underwent facile migratory insertion while the benzyl analogue (**1**: R = CH_2Ph) was reluctant to form the corresponding acyl complex.

In a related series of experiments, Booth and co-workers demonstrated that methyl and phenylmanganese pentacarbonyl complexes (**1**: R^1 = Me or Ph), reactive manganese complexes with regard to migratory insertion, also underwent sequential insertion of carbon monoxide and an alkyne to produce manganacycles **2** (Scheme I) in good yields.[9] However, these authors did not report sequential insertion reactions with less reactive manganese com-

Scheme I



† Dedicated to Lloyd M. Jackman on the occasion of his 60th birthday.
‡ University of Maryland.
§ The Pennsylvania State University.
⊥ University of Delaware.

(1) Preliminary reports on this topic have appeared: (a) DeShong, P.; Slough, G. A. *Organometallics* **1984**, *4*, 636. (b) DeShong, P.; Slough, G. A.; Elango, V. *J. Am. Chem. Soc.* **1985**, *107*, 7788. (c) DeShong, P.; Slough, G. A.; Rheingold, A. L. *Tetrahedron Lett.* **1987**, *28*, 2229. (d) DeShong, P.; Sidler, D. R.; Slough, G. A. *Tetrahedron Lett.* **1987**, *28*, 2232.

0002-7863/88/1510-2575$01.50/0

plexes or alkynes, neither were subsequent transformations of manganacycle **2** described.

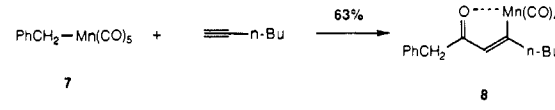
Since alkyl manganese pentacarbonyl complexes (**1**) are readily prepared,[10] we surmised that if the limitations discussed above were overcome, then a new efficient method for the preparation of carbonyl compounds could be developed. Specifically, reaction conditions had to be developed such that unreactive manganese complexes such as benzylmanganese pentacarbonyl (**1**: R = CH_2Ph) would undergo migratory insertion followed by addition of either an alkyne or alkene to form manganacycles **2** or **5**, respectively.

In this paper we report that at pressures of 2–10 kbar a variety of alkylmanganese pentacarbonyl complexes react regioselectively with structurally diverse alkynes or alkenes to produce acyl-coordinated manganese complexes **2** and **5**, respectively, in good yields. These complexes are versatile intermediates for organic synthesis and can be elaborated into *E*-enones (**3**), butenolides (**4**), or ketones (**6**) as outlined in Scheme I.

The results summarized in Table I demonstrate that at high pressures alkylmanganese pentacarbonyl complexes reacted with a variety of alkynes and alkenes by a sequential process involving initial migratory insertion of the alkyl residue to an adjacent carbon monoxide in the metal coordination sphere followed by insertion of the resulting acyl manganese complex into the carbon–carbon multiple bond to afford manganacycles **2** and **5**, respectively. The exceptional stability of these complexes served as a "thermodynamic trap" in the reaction[11] and precluded multiple insertions[3] or β-hydride elimination.[12] For example, methylmanganese pentacarbonyl reacted regiospecifically with electron-deficient alkenes such as α,β-unsaturated ester derivatives and phenyl vinyl sulfone (entries 1–7) affording manganacycles in which the electron-withdrawing group was attached to the same carbon atom as the metal. Similarly, benzylmanganese pentacarbonyl (**7**) which was reported to be reluctant to undergo migratory insertion at atmospheric pressure,[5b,8b,h] also furnished manganacycles under the high-pressure conditions (entries 12–18). It is especially noteworthy that under identical solution conditions, *no adducts were obtained from the reaction of alkenes with manganese complexes when the reaction was performed at atmospheric pressure.*

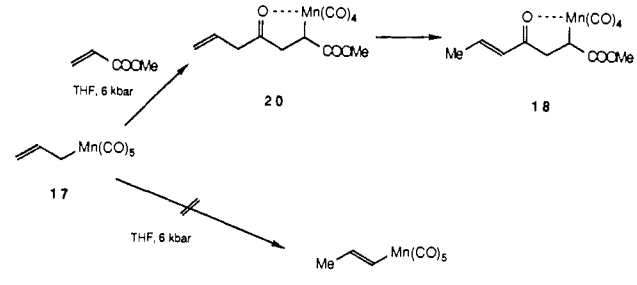
Polymerization of methyl methacrylate (entries 4 and 15) was a serious side reaction in the sequential insertion process and resulted in diminished yields of the corresponding manganacycles. The polymerization of methacrylate could be suppressed by incorporation of 1 mol % of 2,6-di-*tert*-butyl-4-methylphenol (BHT) into the reaction mixture. Addition of larger quantities of BHT did not improve the yield of adducts in these instances. Alkenes such as crotonate and acrylate did not require the incorporation of BHT since these substrates did not undergo polymerization at high pressures.

Unlike alkenes, the reaction of terminal alkynes and methylmanganese pentacarbonyl (**1**: R = Me) gave adducts at atmospheric pressure (entries 9 and 10); however, less reactive manganese complexes required the application of high pressure to produce manganacycles. For instance, reaction of benzylmanganese pentacarbonyl and 1-hexyne failed to give manganacycle **8** after 48 h at atmospheric pressure, whereas a 63% yield of adduct **8** was obtained from the reaction of **7** and 1-hexyne at 6 kbar for 45 h (entry 20).



7 8

Allylmanganese pentacarbonyl (**17**) reacted with methyl acrylate at 6 kbar to give manganese complex **18** (entry 21, Table I) in which the double bond of the allyl moiety had isomerized into conjugation with the ketone. The β,γ-unsaturated adduct **20** was not detected in the reaction mixture, and a control experiment in which the allyl complex was pressurized to 6 kbar in the absence of acrylate did not lead to alkene isomerization to produce vinyl manganese pentacarbonyl complex **19**. Therefore, it was assumed that alkene isomerization was rapid and occurred after insertion of both carbon monoxide and acrylate.



A single manganacycle was obtained in most cases which indicated that addition of the acyl manganese complex to the alkene (or alkyne) had occurred in a stereo- and regiospecific fashion. Confirmation that the addition to the alkene or alkyne had occurred with syn-stereochemistry (entries 2, 7, 12, 14, and 18) was obtained by subsequent transformations of the adducts (vide infra).[1] Ethyl 3-phenylpropynoate (entry 11) was the only sub-

(2) For leading references see: (a) Collman, J. P.; Hegedus, L. A.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA; 1987; pp 356–376. (b) Kuhlman, E. J.; Alexander, J. *Coord. Chem. Rev.* **1980**, *33*, 195. (c) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 88. (d) Davies, S. G. *Organotransition Metal Chemistry: Applications to Organic Synthesis*; Pergamon: Oxford, 1982; pp 348–392. (e) Wender, I.; Pino, P. *Organic Synthesis via Metal Carbonyls*; Interscience; New York, 1977; Vol. 1 and 2. (f) Khan, M. M. T.; Martell, A. E. *Homogeneous Catalysis by Metal Complexes*; Academic: New York, 1974; Vol. 1.

(3) Sen, A. *Adv. Polym. Sci.* **1986**, *73/74*, 125.

(4) Sen, A.; Lai, T.-W. *J. Am. Chem. Soc.* **1982**, *104*, 3520. Lai, T.-W.; Sen, A. *Organometallics* **1984**, *3*, 866.

(5) (a) Noack, K.; Calderazzo, F. *J. Organomet. Chem.* **1967**, *10*, 101 and references cited therein. Calderazzo, F. *Angew. Chem., Int. Ed.* **1977**, *16*, 299. (b) Calderazzo, F.; Cotton, F. A. *Abstracts of Papers*, 7th I.C.C.C. Meeting, June 1962, Stockholm, Paper 6H7.

(6) Casey, C. P.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1976**, *98*, 1166 and references cited therein.

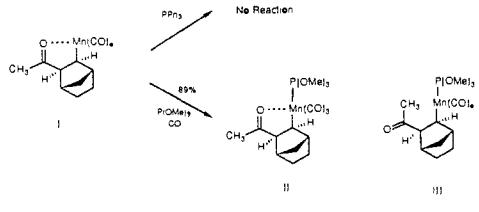
(7) Flood, T. C.; Jensen, J. E.; Statler, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 4410. Flood, T. C. *Top. Stereochem.* **1981**, *12*, 37.

(8) (a) Drew, D.; Darensbourg, M. Y.; Darensbourg, D. J. *J. Organomet. Chem.* **1975**, *85*, 73. (b) Brinkman, K. C.; Vaughn, G. D.; Gladysz, J. A. *Organometallics* **1981**, *1*, 1056. (c) Halpern, J. *Acc. Chem. Res.* **1982**, 15, 332 and references cited therein. (d) Kuty, D. W.; Alexander, J. J. *Inorg. Chem.* **1978**, *17*, 1489. (e) Robertson, J. B.; Whimp, P. O. *Ibid.* **1973**, *12*, 1740 and references cited therein. (f) Keblys, K. A.; Felbey, A. H. *J. Am. Chem. Soc.* **1960**, *82*, 4204. (g) Mawby, R. J.; Basolo, F.; Pearson, R. G. *Ibid.* **1964**, *86*, 5043. (h) Cawse, J. N.; Fiato, R. A.; Pruett, R. L. *J. Organomet. Chem.* **1979**, *172*, 405.

(9) Booth, B. L.; Hargreaves, R. G. *J. Chem. Soc. A* **1970**, 308. See also: Booth, B. L.; Gardner, M.; Haszeldine, R. N. *J. Chem. Soc., Dalton Trans.* **1975**, 1856 and references cited therein. See also: Booth, B. L.; Lewis, E. J. R. *J. Chem. Soc., Dalton Trans.* **1982**, 417 and references cited therein.

(10) Alkylmanganese pentacarbonyl complexes are readily prepared by reaction of alkyl halides with $NaMn(CO)_5$ according to the procedure of Darensbourg.[8a]

(11) Omae has commented upon the exceptional stability associated with five-membered coordination complexes: Omae, I. *Coord. Chem. Rev.* **1980**, *32*, 235 and references cited therein. The exceptional stabillty associated with the coordinated carbonyl group is indicated by the following results. Treatment of complex i[1a] with triphenylphosphine failed to displace the acyl moiety; whereas, i reacted with trimethyl phosphite to produce complex ii. Rather than displace the carbonyl oxygen to give iii, complex i underwent loss of a carbon monoxide ligand.



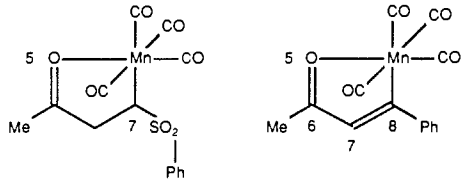
i ii iii

(12) Marsi, M.; Brinkman, K. C.; Lisensky, C. A.; Vaughn, G. D.; Gladysz, J. A. *J. Org. Chem.* **1985**, *50*, 3396.

strate investigated that gave a mixture of regioisomeric manganacycles. In this instance, the presence of two electron-withdrawing groups attached at the alkyne termini led to decreased regiochemical discrimination.

The regiochemistry of addition of the acyl manganese residue to the alkene or alkyne moiety was deduced from the ^{13}C NMR spectra of the respective manganese complexes and by subsequent transformations of the manganacycles (vide infra). For example, the adduct obtained from the reaction of phenylacetylene and methylmanganese pentacarbonyl (entry 9, Table I) displayed olefinic carbon signals at δ 210 (ORD, singlet) and δ 140 (ORD, doublet) indicative of the assigned regiochemistry.[1]

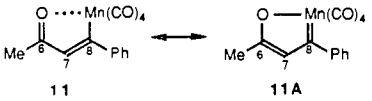
X-ray analysis of adducts **9** and **11** arising from the reaction of methyl manganese pentacarbonyl with phenyl vinyl sulfone and phenylacetylene (Table I, entries 3 and 9), respectively, showed that both complexes had a slightly distorted octahedral geometry about manganese with the acyl group acting as one ligand forming a five-membered array. The five-membered manganacycle ring in complex **9** had an O_5–Mn–C_7 angle of 86.5° and a puckered five-membered ring. This distortion of the bond angle around manganese allowed the other ligands on the metal to compensate and adopt bond angles that were slightly larger than 90°.



9 **11**

The O_5–Mn–C_3 bond angle in complex **11** was reduced even further to 79.2° and reflects the severe geometric constraints imposed by the additional degree of unsaturation in the five-membered ring.

Examination of the bond distances in complexes **9** and **11** revealed an additional structural feature that had important implications with regard to the chemistry of the respective complexes (vide infra). The Mn–C_7 bond distance in complex **9** is 2.148 Å, a value appropriate for an Mn–C_7 single bond.[13] On the other hand, the bond length of the Mn–C_8 bond in unsaturated complex **11** is significantly shorter (2.04 Å) than the corresponding bond



11 **11A**

in **9** and suggests that this bond has partial double bond character as indicated by resonance form **11A**. Manganese carbene complexes in which there is a formal manganese–carbon double bond have been shown to have metal–carbon bond lengths of 1.89–1.99 Å.[13] Structural evidence for resonance form **11A** is important since **11A** is invoked to explain subsequent chemical transformations of this complex. Additional support for the importance of **11A** is that the C_6–C_7 bond length in **11** is virtually identical with the C_7–C_8 bond length suggesting that the C_6–C_7 and C_7–C_8 bonds have partial double bond character as required by **11**/**11A**.

The X-ray data strongly indicated that resonance structure **11A** was the more appropriate representation of the alkyne-derived manganacycle. However, **11A** can also be considered to be an aromatic system, a metallafuran derivative, in which 4 π-electrons are furnished by the organic ligand and 2 electrons are donated from a filled d-orbital on the metal. Hoffmann and Thorn have investigated computationally metallacyclopentadiene complexes and concluded that they did not display aromatic character.[14] However, metallafuran complex **11**/**11A** has not been studied in this regard. Additional support for the hypothesis that manganacycle **11** possesses aromatic stabilization will be discussed in the section pertaining to chemical reactivity of these complexes.

Manganese complexes **2** and **5** are versatile intermediates for the preparation of 1,4-dicarbonyl compounds, enones, and butenolides as evidenced by the results compiled in Table II. Photolytic demetalation of the adducts derived from alkenes proceeded in good yield to afford ketones (entries 1–4, Table II). The two-step procedure of manganacycle **5** formation followed by demetalation is an efficient and general method for the preparation of carbonyl systems and should have applicability in organic synthesis.[1]

The mechanism of the photodemetalation reaction has not yet been rigorously defined; however, several key features of the process have been elucidated. First, the photoreaction proceeded readily when the reaction solvent was acetonitrile. However, the rate and yields of product were not altered by performing the photolysis in mixtures of 1:1 acetonitrile–toluene, 1:1 acetonitrile–diisopropyl ether, or 1:1 acetonitrile–chloroform.

A second feature of the photolysis reaction was that the reaction solvent does not furnish the hydrogen atom that replaces the manganese tetracarbonyl moiety in complex **5**. Photolysis of manganese complex **15** in acetonitrile-d_3 or in a 1:1 mixture of acetonitrile-d_3–deuteriochloroform (CD_3CN–$CDCl_3$) yielded methyl 4-oxo-5-phenylpentanoate (**22**) which had incorporated <1% of the theoretical amount of deuterium. On the other hand, if the photolysate was quenched by addition of D_2O, then excellent incorporation of deuterium into the ketone was observed. This surprising result demonstrated that the demetalation did not proceed via a homolytic cleavage process, otherwise, acetonitrile or chloroform would have furnished deuterium to the product. Instead, the demetalation protocol afforded an anionic intermediate that underwent protonation by water during workup.

The initial reaction of the photodemetalation process involved extrusion of a carbon monoxide ligand as indicated by the following experiments. Photolysis of a 0.02 M acetonitrile solution of complex **15** was performed under three sets of conditions: (a) at a pressure of 0.5–1.0 Torr of argon, (b) at 760 Torr of argon, and (c) at 760 Torr of carbon monoxide. At reduced pressure, photolysis of **15** was complete within 1.5 h and ketone **22** was isolated in 75% yield. However, under an argon atmosphere of 760 Torr, the rate of photolysis was retarded and after 24 h only 40% of complex **15** had undergone demetalation. Even more dramatic, photodemetalation of complex **15** was completely inhibited by an atmosphere of carbon monoxide. *Complex* **15** *was recovered unchanged after 24 h of photolysis under the carbon monoxide atmosphere.* This set of experiments indicated that the first step in the demetalation reaction was loss of carbon monoxide from manganese complex **15**.

The final feature concerning the demetalation reaction that has been recognized was that oxygen was required to liberate the organic ligand from the metal. Photolysis of **15** under vacuum in the absence of oxygen did not produce ketone **22**. The reaction mixture must be opened to air and only then was the ketone produced.

Taken together, these observations suggest that the photodemetalation reaction proceeded as shown in Scheme II. Photolysis of **15** in acetonitrile led to replacement of the carbon monoxide ligands by acetonitrile to produce complex **21**, a coordinatively unsaturated carbon bound η^1-manganese complex. Complex **21** may be in equilibrium with either the η^3-complex or the O-η^1-complex, a manganese enolate, as depicted in Scheme II. Replacement of the carbon monoxide ligands by acetonitrile made the metal susceptible to oxidation, and upon exposure to oxygen and water the metal was oxidized and the organic ligand expelled.

In the case of the adducts arising from alkynes, the demetalation was accomplished by treatment of the manganacycles **2** with protic acid. The resulting enone was often accompanied by formation of a butenolide derivative from insertion of a second molecule of carbon monoxide (entries 1–7, Table III). The second carbon monoxide insertion occurred only with adducts derived from alkynes and suggested that the alkyne-derived manganacycles **2**

(13) Schubert, U. *Transition Metal Carbene Complexes*; Weinheim: Verlag Chemie, 1983; pp 73–111 and references cited therein.
(14) Hoffman, R.; Thorn, D. L. *Nouv. J. Chem.* **1979**, *3*, 39.

Table I. Formation of Manganacycles

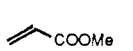
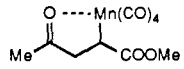
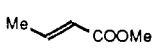
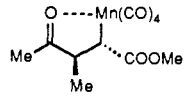
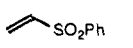
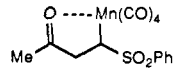
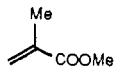
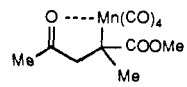
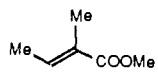
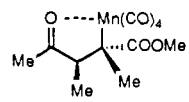
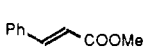
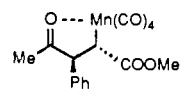
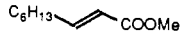
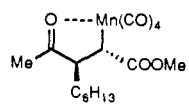
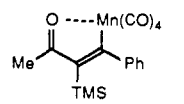
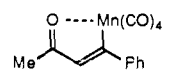
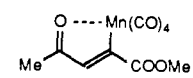
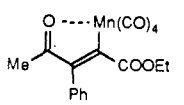
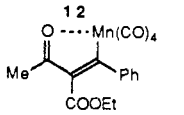
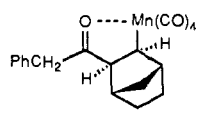
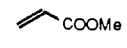
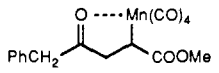
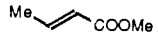
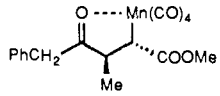
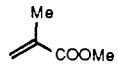
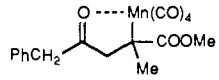
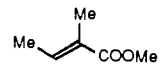
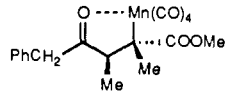
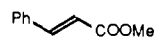
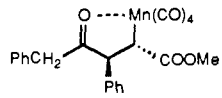
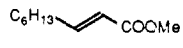
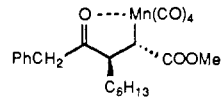
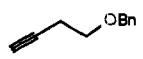
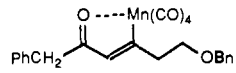
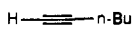
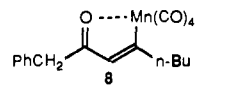
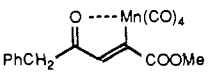
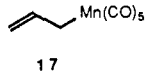
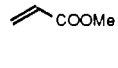
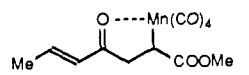
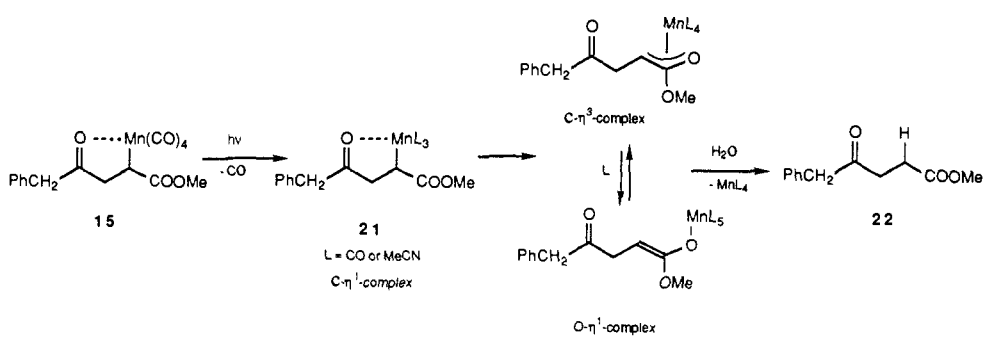
Entry	Alkylmanganese Complex	Alkene/ Alkyne	Conditions [b]	Pressure	Manganacycle	Yield (%) [a]
1	$Me-Mn(CO)_5$ **1**		A	6 kbar		90
2	**1**		A B	6 kbar 5 kbar		53 70
3	**1**		A	6 kbar	 **9**	90
4	**1**		B C D D	5 kbar 2 kbar 5 kbar 7 kbar		25 33 56 63
5	**1**		B B	5 kbar 10 kbar		0 0
6	**1**		B	5 kbar		0
7	**1**		B B	5 kbar 7 kbar		31 57
8	**1**		A	6 kbar	 **10**	72
9	**1**		E	1 bar	 **11**	67
10	**1**		B E	5 kbar 1 bar		81 93
11	**1**		A	6 kbar	 **12**  **13** **12:13** = 1.5:1	87[c]
12	$PhCH_2-Mn(CO)_5$ **7**		A	6 kbar	 **14**	83

Table I (continued)

Entry	Alkylmanganese Complex	Alkene/ Alkyne	Conditions[b]	Pressure	Manganacycle	Yield (%)[a]
13	7		A	6 kbar	 **15**	88
14	7		A B	6 kbar 7 kbar		56 67
15	7		C B D D	2 kbar 5 kbar 5 kbar 7 kbar		4 28 35 55
16	7		B B	5 kbar 10 kbar		0 0
17	7		B	5 kbar		0
18	7		B B	5 kbar 7 kbar		21 63[d]
19	7		A	6 kbar		49
20	7		A	6 kbar	 **8**	63
21	7		B	5 kbar		94
22	 **17**		A	6 kbar	 **18**	70

[a] Isolated yield of purified (>95%) material. [b] Conditions: (A) 48 h/THF; (B) 72 h/Et_2O; (C) 144 h/Et_2O; (D) 72 h/Et_2O/1 mol % BHT; (E) 12 h/THF. [c] Combined yield of **12** and **13**. [d] Combined yield for insertion and demetalation.

Scheme II

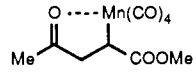
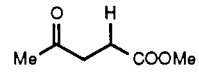
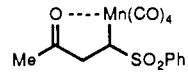
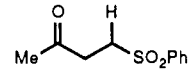
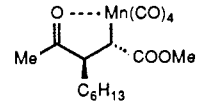
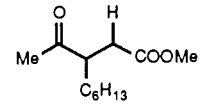
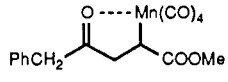
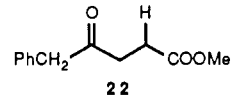
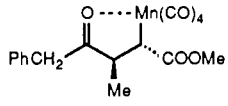
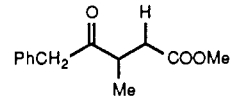
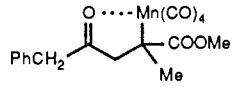
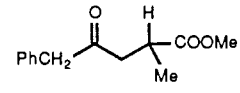
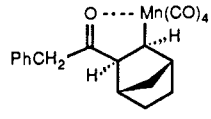
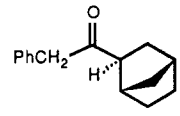
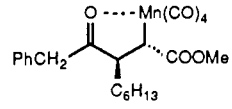
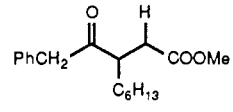
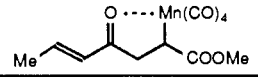
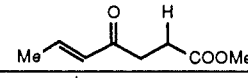


displayed enhanced reactivity due to the intermediacy of cationic manganese complex **23** formed by protonation of manganacycle **11** on the olefinic carbon β to manganese as depicted in Scheme III.

Three pieces of evidence supported this mechanistic hypothesis. First, the X-ray structure of manganacycle **11** (vide supra) displayed an exceptionally short Mn–C_8 bond and longer than expected C_7–C_8 bond indicative of the manganese carbene resonance structure **11A**. Manganacycle **11A** would be expected to protonate on the carbon atom β to the metal (**23**) as discussed above.

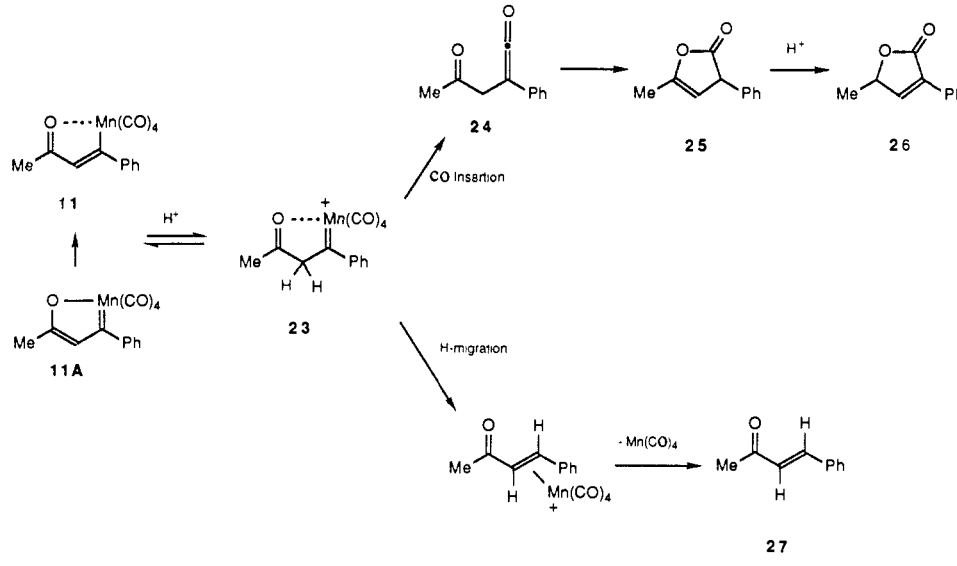
Treatment of manganacycle **11** with DCl instead of HCl under the demetalation conditions, followed by isolation of unreacted

Table II. Demetalation of Saturated Manganacycles[a]

Entry	Manganacycle	Product	Yield (%)[b]
1			>80[c]
2	 **9**		66
3			98
4		 **22**	75
5			98
6			95
7	 **14**		62
8			95
9			82

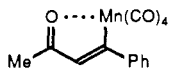
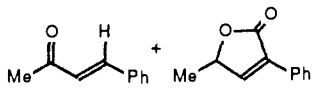
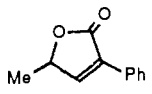
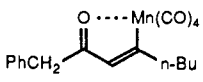
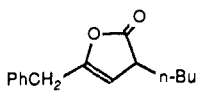
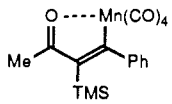
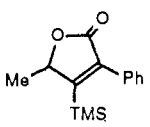
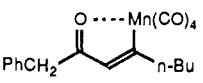
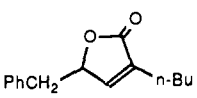
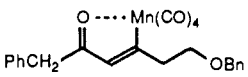
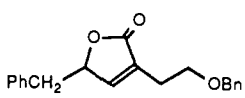
[a] Conditions: Sealed tube, 10 Torr, CH_3CN, 350 nm, 1–10 hr room temperature. [b] Isolated yield of purified (>95%) material. [c] Yield estimated from ^1H NMR containing internal standard.

Scheme III

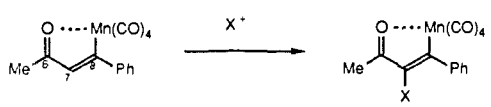


manganese complex **11**, resulted in deuterium incorporation to produce manganacycle **28**. This result indicated that reversible protonation at C_7 of **11** had occurred under demetalation conditions.

Table III. Demetalation of Unsaturated Manganacycles

Entry	Manganacycle	Conditions[a]	Product	Yield (%)[b]
1	 **11**	A		61:19
2	**11**	B	,, ,,	24:38
3	**11**	C		37
4		A		57
5		C		62
6		C		52
7		C		57

[a] Conditions: (A) 3.7% HCl, CH_3CN, 36–72 h, room temperature. (B) 3.7% HCl, CH_3CN, 36–72 h, room temperature, 65 atm CO. (C) DIBAL–*n*-BuLi complex, Et_2O, −80 °C, 1.0 h. [b] Isolated yield of purified (>95%) material.

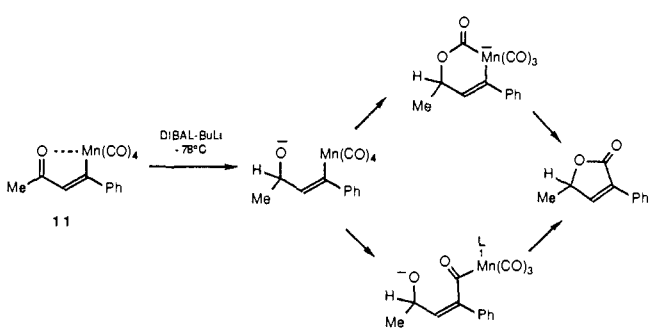


11 **28**: X = D; **29**: X = Br

The propensity for electrophiles to attack at C_7 of complex **11** extended to halogens also. Manganacycle **11** reacted with *N*-bromosuccinimide to produce complex **29** in 94% yield. Introduction of bromine occurred by a mechanism analogous to the protonation sequence shown in Scheme III. This bromination sequence is analogous to electrophilic substitution processes observed in aromatic systems and lends additional support to the hypothesis that manganacycle **11** possess aromatic properties. As expected from an aromatic system, continued exposure of manganacycle **29** to the bromination medium failed to result in further reaction. The carbon–manganese bond is stabilized by incorporation into the aromatic system and resists cleavage by electrophilic reagents.

Partitioning of manganese carbene complex between the CO insertion and H-migration manifolds resulted in formation of the observed products, either butenolide **26** or enone **27**. Insertion of carbon monoxide into the cationic manganese carbene complex **23** generated ketene **24**[15] which after enolization, cyclization, and alkene isomerization gave the observed butenolide. Alternatively, **23** suffered hydrogen migration to provide a cationic manganese–alkene complex. Demetalation of the alkene complex resulted in formation of enone **27** (Scheme III). Helquist,[16] Casey,[17] and Gladysz[18] have observed analogous hydrogen migrations in cationic iron and rhenium complexes, respectively.

Comparison of entries 1 and 2 in Table III demonstrates that the partitioning of complex **23** into the two reaction manifolds can be influenced by performing the reaction in the presence of carbon monoxide. As expected, in the presence of 57 atm of carbon monoxide, the relative amount of lactone **26** increased at the expense of the enone product.



Treatment of the manganese complexes **2** derived from alkynes with a hydride source led to reduction of the carbonyl group and subsequent insertion of a second molecule of carbon monoxide to yield butenolides by an intramolecular version of the Reppe

(15) Insertion of carbon monoxide into chromium carbene complexes has been reported: Yamashita, A.; Scahill, T. A. *Tetrahedron Lett.* **1982**, *23*, 3765.

(16) Kuo, C.-H.; Helquist, P.; Kerber, R. C. *Organometallics* **1984**, *3*, 306.

(17) Casey, C. P.; Miles, W. H.; Tukada, H.; O'Connor, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 3761.

(18) Halton, W. G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6157.

(19) Mullen, A. *React. Struct.: Concepts Org. Chem.* **1980**, *11*, 243–308.

(20) Kims, S.; Anh, K. H. *J. Org. Chem.* **1984**, *49*, 1717.

(21) $LiBEt_3H$ and DIBAL could also be used in this reaction; however, a significant quantity of laciol was obtained in addition to the desired lactone.

(22) Frenz, B. A. 1982 (SDP Plus), Enraf-Nonius, Delft, Holland.

(23) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321.

reaction (Table III).[19] Presumably, formation of an allylic alkoxide by reduction of the carbonyl group triggered the second insertion of carbon monoxide. Several reducing agents were investigated, but the DIBAL–*n*-BuLi complex[20] gave the best yields of the respective butenolides.[21]

As can be seen by the results above, the sequential insertion of carbon monoxide and either alkenes or alkynes into alkyl manganese pentacarbonyl complexes provided an efficacious strategy for the preparation of highly functionalized carbonyl systems. Additional mechanistic studies and application of this methodology to the total synthesis of natural products are in progress and will be reported in due course.

Experimental Section

Melting points were taken in Kimax soft-glass capillary tubes with a Thomas-Hoover Uni-Melt capillary melting point apparatus (Model 6406K) equipped with a calibrated thermometer.

Proton and carbon magnetic resonance spectra (NMR) were recorded on a Varian Associates analytical NMR spectrometer (Model EM-360) or a Bruker WP-200 or WM-360 Super Con spectrometer. Proton and carbon chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane as an internal standard. Coupling constants (J values) are given in hertz (Hz), and spin multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). The spin multiplicities for off-resonance decoupled (ORD) carbon NMR are indicated in the same manner. It should be noted that only poorly resolved proton NMR spectra could be obtained from some manganacycle complexes. The resolution could be enhanced by using very dilute NMR samples. The deuteriated NMR solvent contained 99.0–99.8% deuterium in the indicated position. Infrared spectra were recorded on a Perkin-Elmer Model 281B diffraction grating spectrophotometer. Peak positions are given in reciprocal centimeters (cm^{-1}) and are listed as very strong (vs), strong (s), medium (m), or weak (w). Mass spectral data were obtained on a Kratos MS-950 double-focusing high-resolution spectrometer or on a Finnigan 3200 twin EI and CI quadrupole mass spectrometer equipped with a Finnigan 6000 computer. X-ray analyses were obtained on either an Enraf-Nonius CAD4 with Mo Kα radiation or a Nicolet R3 diffractometer with Mo Kα radiation. Elemental analyses were performed by Micro-Tech Laboratories, Skokie, IL.

Thin-layer chromatography (TLC) was performed on 0.25-mm Merck silica-coated glass plates with the compounds being identified in one or more of the following ways: UV (254 nm), iodine, sulfuric acid, or H_2SO_4/vanillin charring. Preparative layer chromatography (PLC) was performed on 0.25-, 0.50-, or 2.0-mm Merck silica-coated glass plates with the compounds identified as above. Column chromatography was performed on 70–230-mm silica gel 60 purchased from ICN. Flash chromatography was performed with thick-walled glass columns and medium-pressure silica (Merck 32–63 mm). The solvent systems used are reported in each experimental part. The conditions for Chromatotron purification (Harrison Research Inc., Palo Alto, CA) are reported as thickness of silica gel on rotor and eluant. High-performance liquid chromatography (HPLC) was performed on an IBM LC/9533 ternary gradient liquid chromatograph with an IBM LC/9522 fixed wavelength UV detector and a 4.5 mm × 250 mm IBM cyano column. Gas chromatography was performed on a Hewlett-Packard Model 5890A chromatograph equipped with a 0.20 mm × 25 m cross-linked methyl silicone capillary column and flame ionization detector. Helium was the carrier gas.

All solvents were distilled from $CaCl_2$ unless otherwise noted. Ethyl ether, benzene, and tetrahydrofuran (THF) were distilled from sodium/benzophenone ketyl. Acetonitrile was distilled from CaH_2 and stored under nitrogen.

Manganese carbonyl was obtained from Strem Chemical Co. (catalog no. 25-1330) and was used without further purification. All reactions with sodium (pentacarbonyl) manganate(I) were performed in airless Schlenk glassware under an inert atmosphere. All other chemicals were either distilled or recrystalized prior to use.

All syringes and glassware used in reactions were thoroughly dried in an oven at 150 °C and assembled hot under an inert atmosphere of N_2 (g) or Ar (g), except as noted.

The high-pressure apparatus consisted of a hydraulically pressurized autoclave containing castor oil. Pressures were determined directly from a gauge attached to the autoclave. Details of the reaction apparatus are described elsewhere.[25] The reaction vessel consisted of a disposable tuberculine syringe (3 mL) and a Luer cap.

All photochemical reactions were carried out in a Rayonet Photochemical Reactor equipped with a 350-nm light source. All reaction mixtures exposed to photolysis were thoroughly degassed by 3 freeze–pump–thaw cycles.

General Procedure for the High-Pressure Preparation of Alkene Adducts. A solution of alkylmanganese pentacarbonyl complex (ca. 0.7–0.8 mmol) and alkene (1.05–1.2 equiv) in solvent (1.0 mL) was pressurized as indicated. The reaction mixture was depressurized, the reaction vessel was rinsed with EtOAc, and the combined organics were concentrated in vacuo. Adducts were purified by flash chromatography.

Reaction of Methylmanganese Pentacarbonyl and Methyl Acrylate (Table I, Entry 1). The reaction mixture in THF was pressurized to 6 kbar for 48 h and the adduct was isolated as a yellow powder: R_f = 0.31, 2:1 hexane/EtOAc; 145 mg; isolated (90%); mp 93–95 °C dec; IR (CCl_4) 2900 (w), 2042 (m, sharp), 1987 (vs), 1957 (vs), 1674 (s), 1644 (s), 1150 (s); ^1H NMR ($CDCl_3$) 3.69 (s, 3 H), 3.51 (dd, J = 3.1, 19.1, 1 H), 3.01 (dd, J = 3.1, 7.5, 1 H), 2.87 (dd, J = 7.5, 19.1, 1 H), 2.30 (s, 3 H); ^{13}C NMR ($CDCl_3$) 234.2 (s), 213.5 (s), 212.4 (s), 212.0 (s), 199.6 (s), 84.4 (s), 50.7 (q), 49.9 (t), 28.5 (q), 28.1 (d); mass spectrum, m/z (relative intensity, %) 296 (M^+, 3), 268 (2), 212 (16), 184 (31), 154 (76), 130 (18), 126 (11), 102 (7), 86 (20), 57 (77), 55 (22), 43 (54), 29 (28), 28 (100). Anal. Calcd for $C_{10}H_9O_7Mn$: C, 40.56; H, 3.06. Found: C, 40.59; H, 2.97.

Reaction of Methylmanganese Pentacarbonyl and Methyl Crotonate (Table I, Entry 2). The reaction mixture in THF was pressurized to 6.1 kbar for 47 h and the adduct was isolated as a yellow oil: R_f = 0.48, 1:1 hexane/EtOAc; 123 mg isolated (53% yield); IR (CCl_4) 2965 (m), 2940 (m), 2870 (w), 2830 (w), 2039 (m, sharp), 1980 (s), 1952 (vs. br), 1925 (m, shoulder), 1739 (w), 1678 (s), 1634 (s), 1141 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) 3.60 (s, 3 H), 3.42 (m, 1 H), 2.74 (d, J = 7.0 Hz, 1 H), 2.20 (s, 3 H), 1.33 (d, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) 238.6 (s), 221.2 (s), 213.8 (s), 213.3 (s), 213.2 (s), 182.8 (s), 56.1 (d), 50.7 (d), 39.1 (q), 28.5 (q), 18.3 (q); mass spectrum, m/z (relative intensity, %) 310 (M^+, 1), 226 (17), 198 (24), 168 (89), 140 (7), 95 (27), 69 (15), 55 (26), 43 (36), 41 (14), 28 (100); mass spectrum, m/z 198.0085 (M^+ - 4CO; calcd for $C_7H_{11}O_3Mn$ 198.0089).

Reaction of Methylmanganese Pentacarbonyl and Phenyl Vinyl Sulfone (Table I, Entry 3). The reaction mixture in THF was pressurized to 6 kbar for 70 h and adduct **9** was isolated as a pale yellow powder: R_f = 0.13, 2:1 hexane/EtOAc. Adduct was recrystallized from pentane at −78 °C to give 321 mg (90% yield) of crystals suitable for X-ray analysis: mp 142–144 °C dec; IR (CCl_4) 3400 (w, br), 2905 (w), 2053 (m, sharp), 1989 (vs), 1965 (vs), 1655 (m) cm^{-1}; ^1H NMR ($CDCl_3$) (poor resolution) 7.78 (m, 2 H), 7.55 (m, 3 H), 3.59 (m, 1 H), 2.82 (m, 2 H), 2.23 (s, 3 H); ^{13}C NMR ($CDCl_3$) 231.1 (s), 218.5 (s), 212.9 (s), 212.2 (s), 211.0 (s), 141.2 (s), 132.6 (d), 129.0 (d), 127.3 (d), 55.9 (d), 48.9 (t), 28.5 (q); mass spectrum, m/z (relative intensity, %) 356 (M^+, 0.2), 294 (2), 266 (9), 202 (4), 184 (4), 132 (7), 105 (2), 78 (7), 55 (6), 43 (30), 28 (100).

Reaction of Methylmanganese Pentacarbonyl and Methyl Methacrylate (Table I, Entry 4). The reaction mixture in Et_2O was pressurized to 2 and 5 kbar for 72 h, or to 5 and 7 kbar with 1 mol % BHT for 72 h, and the adduct was isolated as a pale yellow oil: R_f = 0.11, 9:1 hexane/EtOAc; yield 33, 25, 56, and 63%, respectively; IR (CCl_4) 2900 (w), 2080 (m), 1995 (vs), 1980 (vs), 1950 (vs), 1720 (w), 1660 (m), 1640 (m), 1140 (m) cm^{-1}; ^1H NMR (C_6D_6) (poor resolution) 3.56, 2.87, 1.84, 1.54; ^{13}C NMR (C_6D_6) 233.0, 184.5, 58.3, 50.7, 44.4, 27.6, 26.2; mass spectrum, m/z (relative intensity, %) 226 (15), 198 (22), 169 (26), 168 (99), 131 (22), 125 (71), 119 (25), 112 (32), 82 (100); mass spectrum, m/z 198.0090 (M^+ − 4CO; calcd for $C_7H_{11}O_3Mn$ 198.0089).

Reaction of Methylmanganese Pentacarbonyl and Methyl Nonenoate (Table I, Entry 7). The reaction mixture in Et_2O was pressurized to 7 kbar for 72 h, and the adduct was isolated as a pale yellow oil: R_f = 0.18, 9:1 hexane/EtOAc; 156 mg isolated (57%); IR (CCl_4) 2900 (m), 2850 (m), 2070 (m), 1995 (vs), 1980 (vs), 1945 (vs), 1730 (w), 1675 (m), 1635 (m), 1160 (m) cm^{-1}; ^1H NMR (C_6D_6) (poor resolution) 3.63 (s), 3.30 (br), 3.07 (d), 1.29, 1.14, 0.89 (t); ^{13}C NMR (C_6D_6) 237.4, 183.3, 60.2, 50.4, 34.7, 32.6, 31.8, 29.5, 27.2, 26.6, 22.9, 14.2; mass spectrum could not be obtained because of the compound's instability.

Reaction of Benzylmanganese Pentacarbonyl and Norbornylene (Table I, Entry 12). The reaction mixture in THF was pressurized to 3.9 kbar for 45 h and adduct **14** was isolated as a yellow powder: R_f = 0.22, 10:3 hexane/EtOAc; 343 mg isolated (84% yield); IR (CCl_4) 2950 (m), 2918 (w), 2896 (w), 2864 (m), 2030 (m, sharp), 1978 (vs), 1938 (vs), 1629 (m) cm^{-1}; ^1H NMR ($CDCl_3$) (poor resolution) 7.6–6.9 (br m, 5 H), 3.76 (s, 2 H), 3.0–2.5 (br m, 3 H), 2.5–2.1 (br m, 1 H), 1.9–1.1 (br m, 6 H); ^{13}C NMR ($CDCl_3$) 235.0 (s), 222.7 (s), 217.2 (s), 215.0 (s), 211.1 (s), 132.7 (s), 129.0 (d), 128.9 (d), 127.6 (d), 68.2 (d), 46.4 (t), 45.9 (d), 42.6 (d), 42.4 (d), 35.6 (t), 34.4 (t), 29.1 (t); mass spectrum, m/z (relative intensity, %) 380 (M^+, 4), 324 (2), 296 (6), 268 (100), 240 (3), 214 (3), 177 (2), 146 (33), 123 (9), 120 (5), 95 (29), 91 (47), 77 (2), 67 (6), 55

(24) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(25) DeShong, P.; Dicken, C. M.; Perez, J. J.; Shoff, R. M. *Org. Prep. Proc. Int.* **1982**, *14*, 369.

(28), 41 (4), 28 (18).

Reaction of Benzylmanganese Pentacarbonyl and Methyl Acrylate (Table I, Entry 13). The reaction mixture in THF was pressurized to 6.0 kbar for 23 h and adduct **15** was isolated as a bright yellow oil: R_f = 0.39, 2:1 hexane/EtOAc; 288 mg isolated (88% yield based on consumed starting material); IR (CCl_4) 3085 (w), 3062 (w), 3030 (w), 2944 (w), 2910 (w), 2042 (m, sharp), 1988 (vs), 1958 (vs), 1740 (br, shoulder w), 1674 (m), 1636 (m), 1161 (s) cm^{-1}; ^1H NMR ($CDCl_3$) (poor resolution) 7.25 (m, 5 H), 3.71 (s, 2 H), 3.55 (s, 3 H), 2.83 (br t, 1 H), 2.38 (br d, 2 H); mass spectrum, m/z (relative intensity, %) 372 (M^+, 1), 344 (1), 288 (10), 260 (100), 230 (58), 228 (11), 184 (30), 157 (36), 155 (35), 146 (9), 129 (13), 115 (21), 91 (69), 86 (11), 55 (36), 49 (13), 28 (27).

Reaction of Benzylmanganese Pentacarbonyl and Methyl Crotonate (Table I, Entry 14). The reaction mixture in Et_2O was pressurized to 7 kbar for 72 h and the adduct was isolated as bright yellow crystals: R_f = 0.22, 4:1 hexane/EtOAc; 182 mg isolated (67%); IR (CCl_4) 2080 (s), 2000 (s), 1990 (s), 1950 (s), 1680 (w), 1165 (m) cm^{-1}; ^1H NMR (C_6D_6) (poor resolution) 7.14, 6.96, 6.64, 3.59, 2.93, 0.78; ^{13}C NMR (C_6D_6) 236.7, 182.6, 132.1, 130.0, 129.2, 127.8, 115.8, 74.0, 54.7, 50.4, 46.3, 41.5, 38.4, 37.2, 17.5, 16.6; mass spectrum, m/z (relative intensity, %) 274 (M^+ - 4CO, 10), 188 (85), 145 (11), 118 (64), 91 (100), 69 (45); mass spectrum, m/z 386.0194 (M^+; calcd for $C_{17}H_{15}O_7Mn$ 386.0198).

Reaction of Benzylmanganese Pentacarbonyl and Methyl Methacrylate (Table I, Entry 15). The reaction mixture in Et_2O was pressurized to 2 and 5 kbar for 72 h, or to 5 and 7 kbar with 1 mol % BHT for 72 h, and the adduct was isolated as a pale yellow oil: R_f = 0.15, 9:1 hexane/EtOAc; yield, 4, 28, 35, 55%, respectively; IR (CCl_4) 3020 (w), 2940 (m), 2070 (s), 1980 (vs), 1950 (vs), 1890 (vs), 1820 (w), 1740 (w), 1655 (m), 1630 (w), 1135 (m) cm^{-1}; ^1H NMR (C_6D_6) (poor resolution) 7.00, 6.78, 3.54, 3.31, 3.11, 1.94, 1.77.

Reaction of Benzylmanganese Pentacarbonyl and Methyl Nonenoate (Table I, Entry 18). The reaction mixture in Et_2O was pressurized to 7 kbar for 72 h, and the adduct was isolated as a pale yellow oil: R_f = 0.26, 9:1 hexane/EtOAc; 156 mg isolated (57%); IR (CCl_4) 2920 (m), 2080 (m), 1985 (vs), 1950 (vs), 1730 (w), 1680 (m), 1630 (m), 1165 (m) cm^{-1}. No other spectral data could be obtained because of the compound's instability.

Reaction of η^1-Allylmanganese Pentacarbonyl and Methyl Acrylate (Table I, Entry 22). The reaction mixture in THF was pressurized to 4.1 kbar for 47 h and adduct **18** was isolated with radial chromatography as a bright yellow oil: R_f = 0.44, 1:1 hexane/EtOAc; 273 mg isolated (79% yield based on consumed starting material); IR (CCl_4) 3035 (w), 2970 (m), 2940 (m), 2900 (w), 2864 (w), 2037 (m, sharp), 1981 (vs), 1950 (vs, br), 1739 (s), 1674 (s), 1640 (m), 1149 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) 7.22–7.21 (m, 1 H), 6.36–6.10 (m, 1 H), 3.67 (s, 3 H), 3.65–3.61 (m, 1 H), 3.05–2.99 (m, 2 H), 1.93 (dd, 3 H); ^{13}C NMR ($CDCl_3$) 221.6 (s), 219.3 (s), 213.5 (s), 212.3 (s), 212.1 (s), 184.3 (s), 151.2 (d), 128.9 (d), 50.4 (q), 44.6 (t), 28.0 (d), 18.9 (q); mass spectrum, m/z (relative intensity, %) 322 (M^+, 1), 294 (2), 238 (40), 210 (100), 180 (39), 178 (58), 152 (23), 134 (99), 124 (6), 107 (19), 100 (10), 96 (22), 86 (41), 82 (11), 69 (23), 56 (48), 55 (73), 41 (13), 28 (56).

X-ray data for manganacycle 9: formula $C_{14}H_{11}O_7SMn$, MW 356, orthorhombic, space group $Pna2_1$, a = 7.731 (1) Å, b = 17.621 (3) Å, c = 11.506 (5) Å, V = 1567.5 Å^3, Z = 4, D_{calcd} = 1.60 g cm^{-3}, $F(000)$ = 768, Mo Kα radiation I = 0.71073 Å, λ(Mo Kα) = 9.67 cm^{-1}.

A crystal measuring 0.40 × 0.35 × 0.15 mm was used for data collection with an Enraf-Nonius CAD4 diffractometer. Accurate unit cell data and the crystal orientation matrix were determined from a least-squares refinement of the setting angles of 25 reflections with $10 \le \theta \le 15°$. Intensity data were collected in the range $1.6 \le \theta \le 30°$ by the $w/2\theta$ scan method with monochromatic Mo Kα radiation. The intensities of three reflections, chosen as standard, were monitored every 2 h of exposure time and showed no significant variation. Intensities of 1896 unique reflections were measured of which 1877 had $I \ge 2.5\sigma(I)$ and were used in the structure solution and refinement. Data were corrected for Lorentz polarization factors. The linear absorption coefficient was sufficiently small that absorption correction was deemed unnecessary.

The structure was solved by the heavy atom method. Refinement was by the full-matrix least-squares method initially with isotropic vibrations followed by anisotropic thermal vibrations of the non-hydrogen atoms. A difference map at this stage revealed positions of all 11 protons; these were included in the refinement with fixed isotropic temperature factors. The refinement converged with R = 0.053 and $R_w = (\sum wD^2/\sum wF_o^2)$ = 0.072. In the refinement cycles, weights were derived from the counting statistics, $w = 1/(\sigma^2F + 0.07F^2)$,[23] and scattering factors were taken from Cromer and Mann[24] and Stewart, Davidson, and Simpson.[25] A final difference map was free of any significant features. Final fractional coordinates and details of molecular geometry are attached as supplementary data.

X-ray data for manganacycle 11: formula $C_{14}H_9MnO_5$, MW 312.2, monoclinic, triclinic, space group $P2_1/c$, a = 7.558 (1) Å, b = 14.803 (3) Å, c = 12.889 (3) Å, V = 1425.0 Å^3, Z = 4, D_{calcd} = 1.46 g cm^{-3}, $F(000)$ = 116, Mo Kα radiation I = 0.71073 Å, λ (Mo Kα) = 5.42 cm^{-1}.

A crystal measuring 0.21 × 0.21 × 0.31 mm was used for data collection with a Nicolet R3 diffractometer. Accurate unit cell data and the crystal orientation matrix were determined from a least-squares refinement of the setting angles of 25 reflections with $10 \le \theta \le 15°$. Intensity data were collected in the range $4 \le 2\theta \le 45°$ by the $\theta/2\theta$ scan method with monochromatic Mo Kα radiation. The intensities of three reflections, chosen as standard, were monitored every 2 h of exposure time and showed no significant variation. Intensities of 1796 unique reflections were measured of which 1445 had $I \ge 2.5\sigma(I)$ and were used in the structure solution and refinement. Data were corrected for Lorentz polarization factors. The linear absorption correction was deemed unnecessary.

The structure was solved by direct methods with SHELXTL (version 4.1). The first E-map revealed all the non-hydrogen atoms. Initial full-matrix least-squares refinement allowing the atoms isotropic vibrations reduced R to 0.31, which dropped to 0.024 after allowing for anisotropic thermal motion in the refinement. A difference map at this stage revealed positions of all 9 protons; these were included in the refinement with isotropic temperature factors. The refinement converged with R = 0.0475 and $R_w = (\sum wD^2/\sum wF_o^2)$ = 0.0509. In the refinement cycles, weights were derived from the counting statistics, $w = 1/(\sigma^2F + 0.05F^2)$,[23] and scattering factors were taken from Cromer and Mann[24] and Stewart, Davidson, and Simpson.[25] A final difference map was free of any significant features. Final fractional coordinates and details of molecular geometry are included as supplementary material.

General Procedure for the High-Pressure Preparation of Alkyne Adducts. A solution of alkylmanganese pentacarbonyl complex (ca. 0.7–0.8 mmol) and alkyne (1.05–1.2 equiv) in solvent (1.0 mL) was pressurized as indicated. The reaction mixture was depressurized, the reaction vessel was rinsed with EtOAc, and the combined organics were concentrated in vacuo. Adducts were purified by flash chromatography.

Reaction of Methylmanganese Pentacarbonyl and 2-(Trimethylsilyl)-phenylacetylene (Table I, Entry 8). The solution of methylmanganese pentacarbonyl and 2-(trimethylsilyl)phenylacetylene in THF was pressurized to 6.0 kbar for 43.5 h and adduct **10** (241 mg, 72% yield, based on consumed starting material) was isolated as a yellow powder: R_f = 0.67, 3:1 hexane/EtOAc; mp 97–98 °C; IR (CCl_4) 3110–3000 (w), 2950 (w), 2884 (w), 2029 (m, sharp), 1983 (vs, sharp), 1954 (vs), 1650 (w, br), 1410 (m), 1265 (m) cm^{-1}; ^1H NMR ($CDCl_3$) 7.29–6.65 (br m, 5 H), 2.24 (s, 3 H), –0.31 (s, 9 H); mass spectrum (relative intensity, %) 384 (M^+, 1), 328 (8), 300 (17), 272 (100), 244 (25), 217 (27), 159 (12), 156 (12), 130 (13), 73 (18), 55 (12), 43 (7). Anal. Calcd for $C_{17}H_{17}O_5SiMn$: C, 53.12; H, 4.47. Found: C, 53.29; H, 4.41.

Reaction of Methylmanganese Pentacarbonyl and Phenylacetylene (Table I, Entry 9). A solution of methylmanganese pentacarbonyl (140 mg, 0.67 mmol) and phenylacetylene (80.7 μL, 0.73 mmol) was stirred in THF (15 mL) at atmospheric pressure for 4 h and adduct **11** was isolated as a bright orange/yellow powder: R_f = 0.52, 4:1 hexane/EtOAc; the product recrystallized from pentane at –40 °C, 140 mg isolated (67% yield); mp 64–65 °C (lit.[9] mp 64 °C); IR (CCl_4) 3077 (m), 3060 (m), 3010 (m), 2960 (w), 2940 (w), 2041 (s), 1987 (vs), 1955 (vs, br), 1454 (vs), 1369 (m), 1329 (m), 1182 (m) cm^{-1}; ^1H NMR ($CDCl_3$) 7.28 (s, 5 H), 6.89 (s, 1 H), 2.30 (s, 3 H); ^{13}C NMR ($CDCl_3$) 251.3 (s), 219.3 (s), 214.3 (s), 210.5 (s), 149.4 (s), 135.3 (d), 128.5 (d), 128.3 (d), 125.2 (d), 26.4 (q); mass spectrum, m/z (relative intensity, %) 312 (M^+, 7), 256 (7), 228 (15), 200 (100), 172 (3), 156 (5), 132 (4), 103 (4), 80 (4), 70 (34), 55 (48), 43 (19), 28 (6); mass spectrum, m/z 311.9835 (M^+, calcd for $C_{14}H_9O_5Mn$ 312.1500), 200.0024 (M^+ - 4CO, calcd for $C_{10}H_9OMn$ 200.1100).

Reaction of Methylmanganese Pentacarbonyl and Methyl Propiolate (Table I, Entry 10). A solution of methylmanganese pentacarbonyl and methylpropiolate in Et_2O was pressurized to 5 kbar or kept at atmospheric pressure for 72 h and the adduct was isolated as a yellow oil. R_f = 0.45 in 4:1 hexane/EtOAc; IR (CCl_4) 3000 (w), 2950 (w), 2090 (m), 2000 (vs), 1960 (vs), 1720 (m), 1325 (m), 1200 (m) cm^{-1}; ^1H NMR ($CDCl_3$) 7.15 (s, 1 H), 3.86 (s, 3 H), 2.38 (s, 3 H); ^{13}C NMR ($CDCl_3$) 231.5 (s), 218.6 (s), 216.7 (s), 213.1 (s), 208.4 (s), 175.2 (s), 135.0 (d), 51.8 (q), 27.2 (q), quaternary carbon not observed.

Reaction of Methylmanganese Pentacarbonyl and Ethyl 2-Phenylpropynoate (Table I, Entry 11). The solution of methylmanganese pentacarbonyl and ethyl 2-phenylpropynoate in THF was pressurized to 6.0 kbar for 40.5 h and adducts **12** and **13** were separated in a 1.5:1 ratio as orange/yellow powders: R_f = 0.28 and 0.21, respectively, in 2:1 hexane/CH_2Cl_2. Less polar isomer, **12** (184 mg, 55% yield): IR (CCl_4) 3080–3040 (w), 2990–2890 (w), 2039 (m, sharp), 1987 (s), 1960 (vs, br), 1925 (w, shoulder), 1700 (s), 1440 (m), 1371 (m), 1322 (m), 1050 (m)

cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.28 (m, 5 H), 3.90 (q, J = 6, 2 H), 2.67 (s, 3 H), 0.79 (t, J = 6, 3 H). More polar isomer, **13** (123 mg, 32% yield): IR (CCl_4) 3100–3040 (vw), 2990–2930 (w), 2043 (m, sharp), 1985 (m, shoulder), 1962 (vs), 1708 (m), 1210 (m), 1166 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.22 (m, 5 H), 4.14 (q, J = 7, 2 H), 2.26 (s, 3 H), 1.09 (t, J = 7, 3 H).

Reaction of Benzylmanganese Pentacarbonyl and *O*-Benzyl-3-butyn-1-ol (Table I, Entry 19). The solution of benzylmanganese pentacarbonyl and *O*-benzyl-3-butyn-1-ol in THF was pressurized to 4.5 kbar for 25 h and adduct **16** (31 mg, 38% yield, based on consumed starting material) was isolated as a dark yellow oil: R_f = 0.43, 8:1 hexane/EtOAc; IR (CCl_4) 3100–3000 (w), 2960–2800 (w), 2037 (m, sharp), 1986 (s), 1941 (vs), 1460 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.54–7.05 (br m, 10 H), 6.97 (s, 1 H), 4.51 (s, 2 H), 4.00–3.60 (br m, 4 H), 3.42 (t, 2 H).

Reaction of Benzylmanganese Pentacarbonyl and 1-Hexyne (Table I, Entry 20). The solution of benzylmanganese pentacarbonyl and 1-hexyne in THF was pressurized to 6.0 kbar for 17.5 h and adduct **8** (82 mg, 63% yield, based on consumed starting material) was isolated as a dark yellow oil: R_f = 0.63, 15:1 hexane/EtOAc; IR (CCl_4) 3025 (w), 2958 (w), 2924 (w), 2860 (w), 2060 (m, sharp), 1990 (s), 1945 (vs), 1645 (m, br) cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.21 (m, 5 H), 6.80 (s, 1 H), 3.77 (s, 2 H), 3.08 (t, 2 H), 1.50 (m, 4 H), 0.90 (m, 3 H).

Reaction of Benzylmanganese Pentacarbonyl and Methyl Propiolate (Table I, Entry 21). A solution of benzylmanganese pentacarbonyl and methyl propiolate in Et_2O was pressurized to 5 kbar for 72 h, and the adduct was isolated as an orange oil: R_f = 0.58, 2:1 hexane/EtOAc; IR (CCl_4) 3020 (w), 2940 (w), 2080 (m), 1990 (s), 1950 (vs), 1700 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.33 (m, 3 H), 7.13 (m, 2 H), 7.10 (s, 1 H), 3.92 (s, 2 H), 3.85 (s, 3 H); ^{13}C NMR ($CDCl_3$) 232.6 (s), 218.5 (s), 216.9 (s), 213.0 (s), 208.3 (s), 175.0 (s), 135.8 (d), 133.2 (s), 129.0 (d), 127.5 (d), 51.7 (q), 47.1 (t); mass spectrum, m/z (relative intensity, %) 370 (M^+, 11), 339 (7), 314 (12), 286 (12), 258 (100).

General Procedure for Demetalation of Alkene-Derived Manganacycles. A solution of manganacycle (ca. 75 mg) in acetonitrile (30 mL) was degassed three times by the freeze–pump–thaw method, sealed under partial vacuum (ca. 10 Torr), and irradiated at 350 nm for 1–20 h. The solution was vented to air and allowed to stir with water (0.5 mL) for 1.5 h. After being concentrated in vacuo, the residue was dissolved in ether and the insoluble material was filtered on a silica pad (1.5 g). The eluent was concentrated in vacuo and the ketone was purified by preparative layer or flash chromatography.

Demetalation of Manganacycle 9 (Table II, Entry 2). The solution of manganacycle **9** was irradiated for 16.5 h and the sulfone (17 mg, 66% yield) was isolated as a white crystalline compound: R_f = 0.16, 1:1 hexane/EtOAc. The ketone was recrystallized from ether: mp 89–90 °C; IR (CCl_4) 3060 (w), 2925 (m), 1726 (s), 1321 (s), 1139 (vs), 888 (vs) cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.90 (m, 2 H), 7.61 (m, 3 H), 3.38 (t, J = 8.0, 2 H), 2.94 (t, J = 8.0, 2 H), 2.19 (s, 3 H). Anal. Calcd for $C_{10}H_{12}O_3S$: C, 56.57; H, 5.71. Found: C, 56.53; H, 5.53.

Demetalation of Manganacycle (Table II, Entry 3). A solution of the manganacycle was irradiated for 1.5 h and the ketone was isolated as a colorless oil (98% yield): R_f = 0.18, 9:1 hexane/EtOAc; IR (CCl_4) 2950 (s), 2930 (s), 2850 (s), 1735 (vs), 1715 (s), 1430 (m), 1160 (vs) cm^{-1}; ^{1}H NMR ($CDCl_3$) 3.61 (s, 3 H), 2.93 (m, 1 H), 2.70 (dd, J = 16.7, 9.7, 1 H), 2.31 (dd, J = 16.7, 4.4, 1 H), 2.19 (s, 3 H), 1.7–1.1 (m, 13 H), 0.84 (t, J = 6.8, 3 H); ^{13}C NMR ($CDCl_3$) 210.6, 172.9, 51.6, 48.0, 35.0, 31.5, 31.3, 29.3, 29.2, 26.8, 22.5, 13.9; mass spectrum, m/z (relative intensity, %) 214 (M^+, 1), 183 (16), 130 (100), 98 (69); mass spectrum, m/z 214.1565 (M^+; Calcd for $C_{22}H_{22}O_3$ 214.1569).

Demetalation of 15 (Table II, Entry 4). The solution of manganacycle **15** was irradiated for 3 h and ketone **22** (14.4 mg, 75% yield) was isolated as a colorless oil: R_f = 0.18, 2:1 hexane/EtOAc. The ketone was purified further by bulb-to-bulb distillation at 128–133 °C (2 Torr): IR (CCl_4) 3090 (w), 3070 (w), 3039 (m), 2980 (m), 1748 (vs), 1727 (vs) cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.29 (m, 5 H), 3.75 (s, 2 H), 3.66 (s, 3 H), 2.77 (t, J = 7.1, 2 H), 2.57 (t, J = 7.1, 2 H). Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.87; H, 6.86. Found: C, 69.95; H, 6.85.

Demetalation of Manganacycle (Table II, Entry 5). A solution of the manganacycle was irradiated for 4.0 h and the ketone was isolated as a colorless oil (98% yield): R_f = 0.22, 4:1 hexane/EtOAc; IR (CCl_4) 3050 (w), 2950 (w), 1735 (vs), 1710 (s), 1430 (m), 1160 (vs) cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.3 (m. 5 H), 3.84 (s, 2 H), 3.62 (s, 3 H), 3.16 (m, 1 H), 2.79 (dd, J = 16.8, 9.0, 1 H), 2.31 (dd, J = 16.8, 5.2, 1 H), 1.11 (d, J = 7.2, 3 H); ^{13}C NMR ($CDCl_3$) 210.1, 172.6, 134.1, 129.6, 128.6, 126.9, 51.6, 48.5, 41.4, 37.0, 16.8; mass spectrum, m/z (relative intensity, %) 220 (M^+, 3), 189 (12), 129 (90), 91 (67), 59 (100); mass spectrum, m/z 220.1079 (M^+; Calcd for $C_{13}H_{16}O_3$ 220.1099).

Demetalation of Manganacycle (Table II, Entry 6). A solution of the manganacycle was irradiated for 1.5 h and the ketone was isolated as a colorless oil (95% yield): R_f = 0.30, 4:1 hexane/EtOAc; IR (CCl_4) 3000 (w), 2950 (w), 1720 (br), 1525 (s), 1200 (m), 800 (s), 700 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.2 (m, 5 H), 3.71 (s, 2 H), 3.65 (s, 3 H), 2.92 (m, 2 H), 2.48 (dd, J = 20.7, 8.3, 1 H), 1.13 (d, J = 6.9, 3 H); ^{13}C NMR ($CDCl_3$) 206.1, 176.0, 134.0, 129.4, 128.7, 127.1, 51.8, 50.2, 45.0, 34.7, 17.0; mass spectrum, m/z (relative intensity, %) 220 (M^+, 1), 129 (52), 90 (65), 59 (100); mass spectrum, m/z 220.1094 (M^+; Calcd for $C_{13}H_{16}O_3$ 220.1099).

Demetalation of Manganacycle 14 (Table II, Entry 7). The solution of manganacycle **14** was irradiated for 14 h to produce 13 mg (62% yield) of ketone as a colorless oil: R_f = 0.34, 4:1 hexane/EtOAc; IR (CCl_4) 3082 (w), 3061 (w), 3030 (m), 2957 (s), 2870 (m), 1709 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.29 (m, 5 H), 3.74 (s, 2 H), 2.54 (dd, J = 8.7, 5.5, 1 H), 2.45 (br s, 1 H), 2.28 (br s, 1 H), 1.86 (m, 1 H), 1.79 (m, 2 H), 1.28 (br m, 6 H). Irradiation at δ 2.54 caused the signal at δ 1.86 to collapse to a doublet of doublets (J = 11.0 Hz). Irradiation of δ 1.86 caused the signal at δ 2.54 to collapse to a doublet (J = 7.5 Hz) and the signal at δ 2.28 to sharpen.

Treatment of ketone with 2 N methanolic NaOH (2 mL) for 2 h did not result in epimerization and starting ketone was reisolated unchanged.

Demetalation of Manganacycle (Table II, Entry 8). A solution of the manganacycle was irradiated for 3.5 h and the ketone was isolated as a colorless oil (95% yield): R_f = 0.25, 9:1 hexane/EtOAc; IR (CCl_4) 3020 (w), 2920 (s), 1725 (br), 1440 (s), 1170 (m), 910 (m), 695 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.3 (m, 2 H), 7.22 (m, 3 H), 3.87 (d, J = 16.3, 1 H), 3.82 (d, J = 16.3, 1 H), 3.62 (s, 3 H), 3.09 (m, 1 H), 2.76 (dd, J = 16.9, 9.9, 1 H), 2.38 (dd, J = 16.9, 4.2, 1 H), 1.57 (m, 1 H), 1.38 (m, 1 H), 1.22 (m, 8 H), 0.87 (t, J = 7.0, 3 H); ^{13}C NMR ($CDCl_3$) 209.8, 172.7, 134.1, 129.7, 128.5, 126.9, 51.5, 49.5, 46.8, 35.4, 31.5, 31.4, 29.1, 26.8, 22.5, 13.9; mass spectrum, m/z (relative intensity, %) 290 (M^+, 1), 199 (100), 139 (48), 91 (64); mass spectrum, m/z: 290.1886 (M^+; Calcd for $C_{18}H_{26}O_3$ 290.1882).

Demetalation of Manganacycle 18 (Table II, Entry 9). The solution of manganacycle **18** was irradiated for 4.5 h and the *E*-α,β-unsaturated ketone (13.9 mg, 82% yield) was isolated as a colorless oil: R_f = 0.37, 2:1 hexane/EtOAc; IR (CCl_4) 3025 (w), 2983 (w), 2942 (m), 2840 (w), 1740 (vs), 1700 (s), 1678 (s), 1632 (s), 1432 (s), 1150 (vs) cm^{-1}; ^{1}H NMR ($CDCl_3$) 6.89 (dq, J = 6.8, 15.8, 1 H), 6.16 (dd, J = 1.6, 15.8, 1 H), 3.67 (s, 3 H), 2.87 (t, J = 6.5, 2 H), 2.61 (t, J = 6.5, 2 H), 1.90 (dd, J = 1.6, 6.8, 3 H); mass spectrum, m/z (relative intensity, %) 156 (M^+, 2), 125 (23), 142 (27), 115 (9), 97 (8), 84 (13), 69 (100), 55 (13), 49 (15), 41 (32), 39 (13), 32 (30).

General Procedure for the Acid Cleavage of Unsaturated Manganacycles. A solution of manganacycle (ca. 0.1–0.3 mmol) in acetonitrile (12 mL) was treated with 3.7% aqueous HCl (0.25 mL) and the mixture was stirred at 25 °C under N_2 until starting material was consumed (36–72 h). The reaction mixture was concentrated in vacuo, diluted with ether, and extracted with water. The aqueous layer was rinsed (3 × 10 mL) with ether and the combined organic layers were dried over anhydrous $MgSO_4$ and concentrated in vacuo. The products were isolated by chromatographic methods.

Acidic Cleavage of Manganacycle 11 (Table III, Entry 1). The reaction mixture stirred for 72 h to give 14 mg (61% yield) of *trans*-4-phenyl-3-buten-2-one (R_f = 0.31, 4:1 hexane/EtOAc) as a pale yellow oil, and 5 mg (19% yield) of 2-methyl-4-phenylfuranone (R_f = 0.21) as a pale yellow oil.

Trans enone: IR (CCl_4) 3090 (m), 3070 (m), 3040 (m), 1700 (s), 1679 (vs), 1615 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.41 (br m, 6 H), 6.64 (d, J = 2.4, 1 H), 2.31 (s, 3 H).

Furanone: IR (CCl_4) 3061 (w), 3030 (w), 2959 (m), 2939 (m), 2870 (w), 1769 (vs) cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.86 (m, 2 H), 7.54 (d, J = 1.5, 1 H), 7.40 (m, 3 H), 5.15 (dq, J = 1.5, 6.8, 1 H), 1.52 (d, J = 6.8, 3 H).

Acid Cleavage of Manganacycle 11 under Carbon Monoxide Pressure (Table III, Entry 2). A solution of manganacycle **11** (57 mg, 0.18 mmol) in acetonitrile (6 mL) was placed in Parr apparatus equipped with a stir bar and 0.3 mL of 10% aqueous HCl was added. The system was pressurized to 41 bars of carbon monoxide and evacuated (3×) and finally pressurized to 58 bars of carbon monoxide. The reaction mixture stirred at room temperature for 144 h then was concentrated in vacuo, diluted with ether (15 mL), and extracted with water (5 mL). Aqueous layer was rinsed with ether (2 × 10 mL) and combined organics were dried over anhydrous $MgSO_4$ and concentrated in vacuo. Two products corresponding to *trans*-4-phenyl-3-buten-2-one (7 mg, 27% yield) and 2-methyl-4-phenylfuranone (12 mg, 38% yield) were isolated by flash chromatography with 2:1 hexane/EtOAc.

Acid Cleavage of Manganacycle 8 (Table III, Entry 4). The reaction mixture was stirred for 36 h to give 13 mg (57% yield) of 2-benzyl-4-butylisofuranone as a colorless oil: R_f = 0.30, 8:1 hexane/EtOAc; IR (CCl_4) 3080 (w), 3060 (w), 3025 (w), 2950 (m), 2921 (m), 2860 (w), 1803 (s), 1669 (m); ^{1}H NMR ($CDCl_3$) 7.27 (s, 5 H), 5.07 (s, 1 H), 3.61 (s, 2 H), 3.21 (m, 1 H), 1.76 (m, 1 H), 1.62 (m, 1 H), 1.31 (m, 4 H),

0.87 (m, 3 H); mass spectrum, *m/z* (relative intensity, %) 230 (M^+, 22), 201 (1), 174 (5), 139 (100), 111 (24), 91 (64), 83 (18), 55 (47), 41 (15), 28 (19).

General Procedure for the Preparation of Furanones by DIBAL "ate" Reduction of Unsaturated Manganacycles. To a −80 °C solution of manganacycle (ca. 0.2–0.4 mmol) in ether (15 mL) was added dropwise by cannula a freshly prepared solution of DIBAL–*n*-BuLi complex[21] (1.8 equiv) in ether/hexane (3 mL). After the solution was stirred at −80 °C for 1.0 h, an aliquot of THF (4 mL) was added, and after an additional 0.5 h, the reaction mixture was quenched with 1.5 mL of 10% HCl. After being warmed to room temperature over 0.5 h, the mixture was diluted with ether (10 mL) and water (4 mL) and extracted with ether. The aqueous layer was rinsed with ether (2 × 10 mL) and the combined organics were dried over anhydrous $MgSO_4$ and concentrated in vacuo. The furanone was isolated by chromatographic methods.

Reduction of Manganacycle 11 (Table III, Entry 3). Furanone (11 mg, 37% yield) was isolated by flash chromatography as light yellow oil: R_f = 0.63, 2:1 hexane/EtOAc; IR (CCl_4) 3060 (w), 3030 (w), 2959 (m), 2930 (w), 2868 (m), 1769 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) 7.86 (m, 2 H), 7.54 (d, *J* = 1.5, 1 H), 7.40 (m, 3 H), 5.15 (dq, *J* = 1.5, 6.8, 1 H), 1.52 (d, *J* = 6.8, 3 H); mass spectrum, *m/z* (relative intensity, %) 174 (M^+, 58), 131 (32), 117 (13), 103 (100), 77 (16), 43 (15), 28 (100).

Also produced in this reaction was 4 mg (18% yield) of an inseparable 10:1 mixture of the *cis*- and *trans*-2-methyl-4-phenylbutyrolactone isolated as a colorless oil: R_f = 0.48, 2:1 hexane/EtOAc; ^1H NMR ($CDCl_3$) cis isomer, 7.37 (m, 5 H), 4.63 (ddq, *J* = 6.2, 12.7, 5.3, 1 H), 3.90 (dd, *J* = 12.7, 8.5, 1 H), 2.78 (ddd, *J* = 8.5, 10.4, 5.3, 1 H), 1.99 (ddd, *J* = 10.4, 12.7, 12.7, 1 H), 1.50 (d, *J* = 6.2, 3 H); trans isomer 7.37 (m, 5 H), 4.81 (m, 1 H), 2.54 (m, 1 H), 2.35 (m, 2 H), 1.46 (d, *J* = 6.5, 3 H).

Also isolated from the reaction mixture was 2 mg (18% yield) of (*E*)-4-phenyl-3-buten-2-ol, isolated as a colorless oil: R_f = 0.37, 2:1 hexane/EtOAc; IR (CCl_4) 3620 (m, br), 3080 (m), 3062 (m), 3030 (m), 2970 (m), 2928 (m), 1254 (m, br) cm^{-1}; ^1H NMR ($CDCl_3$) 7.32 (m, 5 H), 6.58 (d, *J* = 15.9, 1 H), 6.26 (dd, *J* = 15.9, 6.3, 1 H), 4.50 (q, *J* = 6.4 1 H), 1.37 (d, *J* = 6.4, 3 H).

Reduction of Manganacycle 10 (Table III, Entry 5). The reaction mixture was stirred at 0 °C for 4.0 h prior to the addition of the THF aliquot. Furanone (9 mg, 62% yield) was isolated by flash chromatography as a colorless oil: R_f = 0.35, 2:1 hexane/EtOAc; IR (CCl_4) 3060 (w), 2959 (m), 2898 (m), 1762 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) (no TMS was added as an internal standard) 7.27 (m, 5 H), 5.07 (q, *J* = 6.8, 1 H), 1.42 (d, *J* = 6.8, 3 H), 0.00 (s, 9 H); mass spectrum, *m/z* (relative intensity, %) 246 (M^+, 100), 231 (4), 217 (15), 203 (37), 159 (9), 129 (11), 91 (13), 73 (56), 43 (2), 28 (37).

Reduction of Manganacycle 8 (Table III, Entry 6). Furanone (22 mg, 52% yield, based on consumed starting material) was isolated as a pale yellow oil: R_f = 0.52, 4:1 hexane/EtOAc; IR (CCl_4) 3060 (w), 3030 (w), 2958 (m), 2928 (m), 2860 (w), 1768 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) 7.25 (m, 5 H), 6.94 (d, *J* = 1.5, 1 H), 5.10 (ddd, *J* = 1.5, 6.2, 6.8, 1 H), 3.11 (dd, *J* = 13.8, 6.2, 1 H), 2.92 (dd, *J* = 13.8, 6.8, 1 H), 2.22 (m, 2 H), 1.45 (m, 2 H), 1.28 (m, 2 H), 0.89 (t, 3 H); mass spectrum, *m/z* (relative intensity, %) 230 (M^+, 21), 203 (0.3), 141 (12), 91 (100), 77 (2), 41 (11), 29 (3).

Reduction of Manganacycle 18 (Table III, Entry 7). Furanone (19.5 mg, 57% yield, based on consumed starting material) was isolated as a pale yellow oil: R_f = 0.44, 2:1 hexane/EtOAc; IR (CCl_4) 3064 (w), 3030 (w), 2929 (m), 2961 (m), 1770 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) 7.25 (m, 5 H), 7.11 (d, *J* = 1.4, 1 H), 5.10 (ddd, *J* = 1.4, 6.4, 7.0, 1 H), 4.49 (s, 2 H), 3.60 (t, *J* = 6.2, 2 H), 3.10 (dd, *J* = 6.4, 13.8, 1 H), 2.89 (dd, *J* = 7.0, 13.8, 1 H), 2.55 (t, *J* = 6.2, 2 H); mass spectrum, *m/z* (relative intensity, %) 308 (M^+, 2), 217 (2), 202 (18), 91 (100).

Deuterium Incorporation into Manganacycle 11. Formation of Manganacycle 28. A solution of manganacycle **11** (61 mg, 0.20 mmol) in acetonitrile-d_3 (4 mL) was treated with 10% aqueous DCl (0.7 mL) and the solution was stirred at 25 °C under N_2 for 112 h. The reaction mixture was concentrated in vacuo and diluted with ether (7 mL), and solid $NaHCO_3$ was added cautiously until gas evolution ceased. The reaction mixture was dried over anhydrous $MgSO_4$ and concentrated in vacuo, and the residue was purified by flash chromatography to give 24.8 mg (41% yield) of manganacycle **11** (R_f = 0.52, 4:1 hexane/EtOAc) and 6.4 mg (32%) of furanone **28**. The ^1H NMR spectrum of the recovered manganacycle **11** showed a 54% deuterium incorporation at C-3 (δ 7.01).

Furanone was isolated as a pale yellow oil consisting of an inseparable mixture of deuterium incorporated products. ^1H NMR spectrum of the furanone showed a 37% deuterium incorporation for the signal at δ 7.55 corresponding to incorporation at the olefinic carbon and a 70% deuterium incorporation at δ 5.16 corresponding to incorporation at the carbon α to the lactone oxygen. Mass spectrum of furanone, *m/z* (relative intensity, %) 175 (M^+, 67), 174 (M^+, 57), 132 (36), 131 (33), 104 (100), 103 (94), 77 (23), 43 (24), 28 (89). Mass spectral analysis indicated a 54:46 ratio of monodeuteriated to dideuteriated products. No *trans*-4-phenyl-3-buten-2-one was formed in the deuterium cleavage reaction.

Bromination of Manganacycle 11. Formation of Manganacycle 29. To a 0 °C solution of manganacycle **11** (210 mg, 0.67 mmol) in methanol (6 mL) was added NBS (17.1 mg, 0.096 mmol) and the mixture was stirred at 0 °C for 0.8 h. The reaction mixture was concentrated in vacuo and manganacycle **29** (33.3 mg, 89% yield) was isolated by flash chromatography as a bright orange solid: R_f = 0.17, hexane; mp 95–96 °C; IR (CCl_4) 3080 (w), 2920 (w), 2050 (m, sharp), 1993 (m), 1968 (vs), 1330 (m, br) cm^{-1}; ^1H NMR ($CDCl_3$) 7.41 (tt, *J* = 7.1, 0.9, 2 H), 7.24 (tt, *J* = 5.4, 1.3, 1 H), 7.08 (dt, *J* = 1.3, 7.1, 2 H), 2.55 (s, 3 H); mass spectrum, *m/z* (relative intensity) 392 (21), 390 (M^+, 21), 336 (20), 334 (19), 308 (41), 306 (42), 280 (98), 278 (100), 238 (54), 236 (55), 156 (41), 144 (25), 136 (26), 134 (26), 129 (81), 75 (9). Anal. Calcd for $C_{10}H_{12}O_5MnBr$: C, 42.99; H, 2.07. Found: C, 43.01; H, 2.03.

Addition of Trimethyl Phosphite to Manganacycle i (Footnote 11). To a solution of manganacycle i (49 mg, 0.16 mmol) in hexane (4 mL) was added trimethyl phosphite (29 mg, 0.24 mmol) and the mixture was stirred at room temperature under N_2 for 17 h. The reaction mixture was concentrated in vacuo and 34 mg (94% yield, based on consumed starting material) of the addition product was isolated by flash chromatography as a yellow solid: R_f = 0.20, 6:1 hexane/EtOAc, mp 79–81 °C; IR (CCl_4) 2945 (m), 2916 (m), 2860 (m), 2842 (w), 1992 (m), 1929 (vs), 1898 (vs), 1638 (s); ^1H NMR ($CDCl_3$) 3.51 (d, *J* = 10.0, 9 H), 2.39 (m, 4 H), 2.08 (s, 3 H), 1.50 (m, 2 H), 1.26 (m, 4 H); ^{31}P NMR ($CDCl_3$) 45.12; mass spectrum, *m/z* (relative intensity, %) 400 (M^+, 6), 344 (0.5), 316 (100), 285 (4), 272 (7), 194 (9), 192 (81), 180 (11), 164 (20), 149 (11), 134 (14), 124 (12), 120 (14), 95 (11), 93 (63). Anal. Calcd for $C_{15}H_{22}O_7PMn$: C, 45.00; H, 5.55. Found: C, 45.21; H, 5.50.

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Supplementary Material Available: Tables of positional parameters and temperature factors for **9** and **11** (3 pages). Ordering information is given on any current masthead page.